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Henkel LOCTITE

HIGH PRODUCTION VOLUME (HPV) CHEMICAL CHALLENGE PROGRAM

TEST PLAN AND ROBUST SUMMARY

for

2-ETHYL CYANOACRYLATE

CAS No. 7085-85-0

Submitted by
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HPV VOLUNTARY PROGRAM

ETHYL CYANOACRYLATE

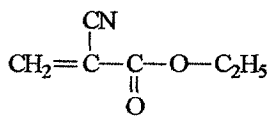
GENERAL INFORMATION

CAS Number
7085-85-0

Chemical Name
Ethyl cyanoacrylate

CAS Descriptor
Propenoic Acid, 2-cyano-, ethyl ester

Structural formula



Quantity
It is estimated that approximately 1,250,000 lbs. of ethyl cyanoacrylate is produced in the United States each year.

Use Pattern

Cyanoacrylates have been used worldwide for over 30 years. They are "instant" adhesives that bond to a variety of substrates including metals and plastics. They are applied as liquids and cure within seconds to minutes at room temperature by reacting in the presence of moisture or weakly alkaline materials forming inert, hard, polymeric solids with virtually no vapor pressure.

Approximately 80% of cyanoacrylate adhesives are the ethyl ester, and the majority of the remainder is the methyl ester. During the manufacture of cyanoacrylate esters, a small concentration of inhibitor is added to prevent polymerization. Additives such as thickeners and colorants and further inhibitors or activators may be added during the formulation of the adhesive to optimize their use for specific applications. A typical cyanoacrylate adhesive comprises 80-95% cyanoacrylate ester, 5-15% thickener, and 0.5-2% inhibitor.

Only a very small quantity is needed to create a bond, therefore the product is usually applied "drop by drop." This use characteristic together with its rapid polymerization to form an inert solid result in a very small potential for environmental damage.

Ethyl cyanoacrylate adhesives are widely used in the consumer and industrial markets.

Industrial applications include:

- The automotive and appliance industry where the major utility is attaching weather-stripping and trim strips, and for positioning rubber gaskets and other parts prior to assembly.
- The electronics industry for speaker magnet bonding, printed circuit boards, small component bonding.
- Manufacture of medical devices including catheters, and tubing.

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Cyanoacrylates are also widely used as consumer adhesives accounting for approximately 50% of the consumer adhesive market. The predominant applications are arts, crafts, and home repairs. They are also used for attaching and repairing artificial fingernails. Consumer cyanoacrylate adhesives are sold in very small packages, mostly 2 or 3-gram tubes or bottles. Thus, the opportunity for over-exposure and injury in the consumer market is small.

TEST PLAN

Ethyl Cyanoacrylate
CAS No. 7085-85-0

STUDY	INFORMATION (Y/N)	OECD Study	GLP	ACCEPTABLE (Y/N)	SIDS TESTING REQUIRED (Y/N)
Physical/Chemical Elements					
Melting Point	Yes	Unknown	Unknown	Yes	No
Boiling Point	Yes	Unknown	Unknown	Yes	No
Vapor Pressure	Yes	Unknown	Unknown	Yes	No
Partition Coefficient	Yes	Yes	Yes	Yes	No
Water Solubility	Yes	Yes	Yes	Yes	No
Environmental Fate and Pathways Elements					
Photodegradation	Yes	N/A	N/A	Yes	No
Stability in Water	Yes	Yes	Yes	Yes	No
Biodegradation	Yes	N/A	N/A	Yes	No
Fugacity	Yes	N/A	N/A	Yes	No
Ecotoxicity Elements					
Acute Fish	Yes	N/A	N/A	Yes	No
Toxicity to Aquatic Plants	Yes	N/A	N/A	Yes	No
Acute Toxicity to Aquatic Invertebrates	Yes	N/A	N/A	Yes	No
Health Elements					
Acute Toxicity	Yes	Equivalent	No	Yes	No
Genetic Tox. in vivo)	Yes	Unknown	Unknown	Yes	No
Genetic Tox. in vitro)	Yes	Unknown	Unknown	Yes	No
Repeat Dose Toxicity	Yes	N/A	N/A	Yes	No
Reproductive Toxicity	Yes	N/A	N/A	Yes	No
Developmental Tox.	Yes	N/A	N/A	Yes	No

JUSTIFICATION

Physical and Chemical Elements
The melting point, boiling point, and vapor pressure of ethyl cyanoacrylate are documented in standard adhesive textbooks. This data is considered adequate and no further testing is proposed. Testing to determine the partition coefficient failed to produce a value because of the reactive nature of the monomer.

Environmental Fate and Pathway Elements
Alkyl cyanoacrylates are among the most reactive monomers known in anionic polymerization. In the atmosphere and in biological systems, the available hydroxyl ions initiate rapid polymerization as evidenced by the rapid bonding to skin by instant adhesives comprising predominantly cyanoacrylate

esters. This property renders ethyl cyanoacrylate a useful adhesive and makes significant exposure to ethyl cyanoacrylate monomer improbable.

The risk of either environmental or biological exposure is further reduced by the manufacture, distribution, and use patterns. Ethyl cyanoacrylate is produced in closed systems and held at the manufacturing site in 55-gallon drums. After it is formulated for commerce, the predominant product size is less than one ounce. The product is used either drop-wise or as a small bead. Thus, an accidental discharge during distribution and use would be limited in size, and therefore neither environmental modeling nor testing is warranted.

Ecotoxicity Elements

For the reasons described in the previous section, the risk exposure of aquatic organisms is extremely limited. Furthermore testing in aquatic animals is not feasible. As detailed in the section on health effects, The National Toxicology Program (NTP) had difficulty in implementing a delivery system for dosing terrestrial animals and recommended that ethyl cyanoacrylate be removed from their priority testing list[1]. We therefore conclude no value would be derived from attempting to test ethyl cyanaocrylate in aquatic organisms.

Health Elements

Data is provided for acute oral and acute dermal toxicity, eye and skin irritation, and acute inhalation toxicity. No additional testing is planned. This is consistent with the position of the Environmental Defense Fund, which on its scorecard has recorded that there is adequate acute toxicity information for ethyl cyanoacrylate.

Reported[2] workplace exposure levels are up to 0.21 ppm for a 40-minute exposure, and an 8-hour time weighted average (TWA) of 0.06 ppm during the manufacture of ethyl cyanoacrylate. The maximum level reported when ethyl cyanoacrylate adhesive was used in a manufacturing process was 0.21ppm for an 8 hour TWA. Levels found in the Loctite manufacturing plant[3] ranged from 0.003 to 1.5 ppm for exposures of 15 minutes or less. Eight-hour time weighted averages were nearly always below 0.1 ppm. The American Conference of Governmental Industrial Hygienists (ACGIH) has established a TLV of 0.2 ppm (8-hour TWA) for ethyl cyanoacrylate. ACGIH has not suggested a short-term exposure limit or a ceiling value for ethyl cyanoacrylate.

Monomeric ethyl cyanoacrylate has an unpleasant acrid odor and is irritating to the eyes and mucous membranes of the nose, throat, and upper respiratory tract. The odor threshold is reported as 1 ppm and the irritation threshold 3-5 ppm[4]. These properties make even occasional exposures to toxic levels of ethyl cyanoacrylate improbable as discomfort propels one to leave any area where the airborne concentration of cyanoacrylate is appreciably above the irritation threshold.

The NTP has completed in-vivo and in-vitro genetic toxicity tests. No further testing in these categories is necessary.

As would be anticipated from this chemistry, dosing animals for repeated dose studies is problematic. Ethyl cyanoacrylate was listed by the Interagency Test Committee as a TSCA 4(e) priority chemical. After preliminary work, NTP[5] recommended its removal from the priority list citing "high reactivity of the chemical and the resulting difficulties in implementing the delivery of an effective concentration of the un-

[1] 60 FR 42987, 1995.
[2] Methyl cyanoacrylate and ethyl cyanoacrylate, Risk assessment document, UK Health and Safety Executive HMSO, Norwich UK, 2000.
[3] Paustenbach, D.,et al, Am. Ind. Hyg. Assoc J., 62, 70-79, 2001.
[4] McGee W.A., et al, Am. Ind. Hyg. Assoc J., 29, 558-561, 1968.
[5] 60 FR 42982-7, 1995

polymerized chemical to the test animals". NTP[1] also reported that they were unable generate a stable aerosol.

The United Kingdom Health and Safety Executive (HSE) has published a Risk Assessment Document on methyl and ethyl cyanoacrylate[2]. This risk assessment concluded that there are no grounds for concern of carcinogenicity at exposures below the threshold for chronic inflammatory responses in tissues at the site of contact. In addressing reproductive toxicity, HSE concluded "due to the reactive nature of ethyl cyanaocrylate, little systemic distribution is predicted following exposure by any physiological route. Furthermore, the overall pattern of toxicity data available suggests that the toxicological effects of ethyl cyanoacrylate would be largely restricted to local site of contact effects on the eyes and respiratory tract." Loctite concurs with these conclusions.

To address concerns that cyanoacrylates, including ethyl cyanoacrylate may act as respiratory sensitizers capable of inducing allergic asthma, Loctite Corporation sponsored two studies. The first was a survey to determine the airborne concentrations of cyanoacrylate in a manufacturing plant[3] and the second was an epidemiological[4] study that investigated the pulmonary effects of repeated occupational exposure to cyanoacrylates. The airborne concentrations determined in the first study provided the basis for the epidemiological study. The epidemiological study provided no evidence that those occupationally exposed to cyanoacrylate vapors during the manufacture and packaging of methyl and ethyl cyanoacrylate adhesives had any chronic pulmonary damage or that ethyl cyanoacrylate acted as a respiratory sensitizer. Subjects who had been exposed for a period of up to 18 years had no increased incidence of pulmonary obstruction compared to an unexposed population.

[1] NTP 1998 Annual report Table 6.
[2] Methyl Cyanoacrylate and Ethyl Cyanoacrylate, Risk Assessment Document, UK Health and Safety Executive HMSO, Norwich UK, 2000.
[3] Paustenbach, D.,et al, Am. Ind. Hyg. Assoc J., 62, 70-79, 2001.
[4] Goodman, M., et al, J. Toxic. & Environ. Hlth Part A, 59, 135-163, 2000.